DEVELOPMENT OF CONTINUOUS SYSTEM BASED ON NANOSCALE ZERO VALENT IRON PARTICLES FOR PHOSPHORUS REMOVAL

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Nanoscale Zero Valent Iron (NZVI) is one of the materials that have gained attention in the field of water treatment and environmental remediation in recent years. The main purpose of this study is to develop and evaluate a phosphorus removal system using NZVI particles. The NZVI used for the experiments was synthesized under optimum conditions using the chemical reduction method. This continuous system consisted of Continuous Stirred Flask Reactor (CSFR), settler, polishing unit, and sand column. The continuous experiment showed that 73.84% phosphorus was removed mainly at CSFR. Further, 80.62% total iron was removed and recycled at the settler. Based on the continuous operation results, there was a strong relationship between iron concentration and ORP value ($R^2 = 0.9969$). This result indicated that ORP would be an important monitoring parameter while operating the continuous system. The aerobic condition contributed the highest phosphorus overall removal efficiency (91.37%) due to the enhancement of iron corrosion. Copper bimetal particles also achieved the highest removal efficiency (94.96%) after increasing the active site and decreasing the solution pH. Finally, comparing the aerobic and bimetallic cases, we concluded that the bimetallic case is the best condition for removing phosphorus because it could treat large solution volume than the aerobic one could.

Key Words : *phosphorus removal, nano-scale zero valent iron (NZVI), continuous system*

1. INTRODUCTION

Phosphorus (P) can be found in the aquatic system in both particulate and dissolved forms. The normal forms of phosphorus in the aqueous system are orthophosphates, polyphosphates, and organic phosphates¹.

Phosphorus, which is a non-renewable, non-interchangeable finite resource, is an important nutrient for living organisms (animals, microbes, plants, and algae)². However, the excessive amount

of phosphorus present in natural waters is known to cause eutrophication³. Xu et al. reported that the eutrophication threshold of total phosphorus (T-P) for freshwaters was from 0.02 to 0.10 mg/L⁴. Eutrophication results in the depletion of oxygen that leads to death of aquatic animals and adverse effects on the aquatic environment. Phosphorus is found in municipal wastewater, industrial wastewater, agricultural drainage (fertilizer), and household wastewater. Therefore, higher concentration of phosphorus wastewater should be treated before be-

ing discharged into the aquatic environment. To remove excessive phosphorus from water, chemical precipitation and enhanced bacteria activity were commonly used⁵⁾.

In chemical precipitation, these chemicals, such as Ca^{2+} ⁶⁾, Al^{3+} ^{7), 8)}, Mg^{2+} ⁹⁾, and Fe^{3+} ¹⁰⁾ were widely used. This is one of the effective methods for removing phosphorus and is suitable where there is low concentration of phosphorus in water. However, if there is high concentration of phosphorus in the water, the system is not suitable because it will require a large amount of chemicals¹¹⁾. Phosphorus removal by using phosphate-accumulating bacteria is also widely used in the wastewater treatment process, but phosphorus removal is limited by bacteria and wastewater conditions. Furthermore, this approach produces excess sludge containing high concentrations of phosphorus and pollutants, such as heavy metals, which are very difficult and costly to treat^{11), 12), 13)}. Both methods are widely used these days; however, both of them have disadvantages.

In recent years, due to the importance of nanotechnologies, Nanoscale Zero Valent Iron (NZVI) has been investigated and used in the removal of not only phosphorus but also several environmental pollutants such as heavy metals^{14), 15), 16)}, nitrate^{17), 18)}, and azo dye¹⁹⁾ from aqueous systems. Due to their morphological shape, NZVI particles have a large specific surface area that provides more active sites for pollutant removal²⁰⁾. Meanwhile, the activity of reaction with phosphorus could be improved since phosphorus easily reacts with iron²¹⁾. Results of phosphorus removal using NZVI experiments have been reported. Almeelbi and Bezbaruah²²⁾ reported that maximum phosphorus adsorption capacity of NZVI was 24.38 mg P/g. Eljamal et al.²³⁾ reported that the maximum adsorption capacity by NZVI/ CuCl_2 had doubled up to 50 mg P/g. It has been reported also that the phosphorus removal efficiency under oxic condition was higher than under anoxic and anaerobic conditions²⁴⁾.

The mechanism of phosphorus removal by NZVI has not yet been perfectly determined. A few researchers said that the main mechanism of phosphorus with NZVI mainly exhibited adsorption and coprecipitation reaction¹¹⁾. However, these reports were mainly focused on the maximum adsorption capacity and its mechanisms by batch experiments. Recently, some reports have focused on the continuous treatment system using NZVI^{25), 26)}. No reports specifically shed light on removing phosphorus by adopting a continuous treatment system using NZVI. The objective of this work is to obtain some optimized conditions for removing phosphorus by NZVI using the continuous system. A total of five different experiments were conducted. Three of them were

conducted for different gaseous phase conditions by using ambient, aerobic, and anaerobic conditions. Two of them were conducted to investigate the CuCl_2 effect for removing.

2. MATERIALS AND METHODS

(1) Chemicals

The following chemical reagents and materials were used: Sodium borohydride (NaBH_4 , 98.0%, Junsei Chemical Co., Japan), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99.0%, Junsei Chemical Co., Japan), potassium dihydrogen phosphate (KH_2PO_4 , 99.5%, Kanto Chemical Co., Japan), and anhydrous copper chloride (CuCl_2 , 99.9%, Aldrich Inc., USA). Nitrogen gas purging was done on all prepared solutions for de-oxygenation. All chemicals were applied as delivered without further purification.

(2) Synthesis of NZVI

NZVI was synthesized following this chemical reaction (Equation (1))²⁷⁾:

Precursor 1 was prepared by dissolving 21.0 g of NaBH_4 in 1,200 mL of deoxygenated deionized water (DIW). Precursor 2 was prepared by dissolving 50.0 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 1,200 mL of DIW in a separate flask. Then precursor 1 was added to precursor 2 using a peristaltic pump at the rate of 16 mL/min. with vigorous stirring at 250 rpm under nitrogen condition at constant temperature of $25 \pm 0.5^\circ\text{C}$ using a water bath. The synthesis was conducted in 5 L four-neck glass flask and left 20 min. for aging to complete the reaction²³⁾. In the case of CuCl_2 bimetallic synthesis, 1.0 g CuCl_2 was added to precursor 2 before mixing with precursor 1²⁸⁾. The synthesized particles were filtered by vacuum filter, washed with DIW three times, and immediately used in the continuous experiments.

(3) Phosphorus solution quality

The KH_2PO_4 was used as a phosphorus source and it was diluted with tap water by up to 25.6 ± 1.2 mg P/L. The phosphorus concentration was fixed in all experiments. Their pH, ORP, and DO were 7.0 ± 0.2 , 0.2 ± 3.5 mV, and 10.2 ± 2.5 mg DO/L, respectively.

(4) Details of the continuous system

The flow diagram of the laboratory-scale continuous system is illustrated in **Fig. 1**. The treatment system consisted of a four-neck flask reactor

Fig.1 The flow diagram of laboratory-scale continuous system.

Table 1 The operation conditions.

Exp. No.	NZVI dosage (g)	CuCl ₂ bimetal or addition	Gaseous phase conditions	Air flow rate (mL/min.)	Solution feeding rate (mL/min.)	Actual initial phosphorus conc. (mg/L)
1	10	-	Ambient	-	20	23.5
2	10	-	Aerobic	1,000 (air)	20	26.1
3	10	-	Anaerobic	1,000 (N ₂)	20	26.1
4	10	Bimetal (1g CuCl ₂ : 10 g NZVI)	Ambient	-	20	26.1
5	10	Addition (1g CuCl ₂ : 10 g NZVI)	Ambient	-	20	26.1

(CSFR), settler, polishing unit, and sand column. The four-neck flask was a glass flask with an effective volume of 5 L. This unit was installed as the main reactor for removing phosphorus. The phosphorus solution was supplied by a peristaltic pump at 20 mL/min. and stirred with an impeller (stirrer) at a speed of 250 rpm to mix the phosphorus solution and NZVI vigorously. The pumped solution and NZVI were first reacted here. Especially only CSFR, the temperature was maintained at 25°C during the water bath. Other reactor temperatures depended on the room temperature. The settler corresponded to the primary settler. Outflowed NZVI from CSFR were settled by gravitation here. The settler was made by

glass with an effective volume of 6.7 L. The settled NZVI was recycled to CSFR by a peristaltic pump at 20 mL/min. There were two reasons for installing the recycle system. The first reason was to prevent the outflow of NZVI from the whole system. Without this unit, the large quantity of iron compounds might outflow. The second reason was to maintain the stability of iron concentration inside the CSFR. Unreacted NZVI can be used in the CSFR and remove phosphorus again.

The polishing unit was installed as a secondary settler to remove the remaining iron compounds. It was made by polypropylene materials with an effective volume of 2.8 L. Five baffles were installed

inside the reactor.

The sand column was installed as a final unit to remove the remaining phosphorus and iron compounds by adsorbing them onto the sand surface. The sand can adsorb dissolved phosphorus and iron compounds²⁹. The sand column body was made by plexiglas with an effective volume of 1.1 L. The silica sand (JIS standard sand, Silica sand No.5) was packed with 1.1 L.

Five different condition experiments were conducted in this study (**Table 1**). In all experiments, NZVI dosage and phosphorus concentration were fixed at 10 g³³) and 25.6 ± 1.2 mg/L²⁹). To obtain enough contact time inside the CSFR and evaluate the effect of several parameters, the longer hydraulic retention time (HRT) was set at four hours. First, in order to investigate the effect of oxygen on phosphorus removal, three of the experiments were conducted under different gaseous phase conditions using ambient, aerobic, and anaerobic conditions. In experiment 1, the gaseous phase condition in the CSFR was kept at ambient condition, and no air injection was conducted. In experiment 2, the gaseous phase condition in the CSFR was kept at aerobic condition. In order to obtain the desired condition inside the CSFR, air was injected during the whole duration of the experiment. An air pump (NISSO CHIKARA @4,000 SW, NISSO Co. Ltd. Japan) was used to inject air. The air flow rate was 1,000 mL/min. In experiment 3, the gaseous phase condition in the CSFR was kept at anaerobic condition by injecting nitrogen gas during the whole duration of the experiment. The nitrogen flow rate was 1,000 mL/min. For experiments 4 and 5, which were conducted under ambient conditions, the effect of CuCl₂ on phosphorus removal was investigated. In the NZVI study field, several heavy metals were reported to have enhanced the reactivity because they provided more active site on the surface of NZVI or they served as reductants^{28), 30)}. The NZVI/CuCl₂ (10.0 g: 1.0 g) bimetallic nano particles²⁸⁾ were used as adsorbents for experiment 4. In experiment 5, 1.0 g CuCl₂ was added to CSFR before beginning the operation²³⁾.

The main difference between experiments 4 and 5 was the manner in which CuCl₂ contributed to removing phosphorus. With respect to the bimetallic case, pure Cu attached on the surface of NZVI and gave more active site. According to previous reports, NZVI/CuCl₂ nanoparticle surface area was 35.1 m²/g. This value was larger than that of pure NZVI (32.6 m²/g)³¹⁾. And with respect to the CuCl₂ addition case, CuCl₂ reaction with NZVI increased iron corrosion on the surface and provided its surface with copper and copper ferrite particles. These copper compounds enhance electric conductivity (EC) of the

surface and support in the sorption of phosphorus molecules by ferrites, ferrous hydr(oxides), and ferric hydr(oxides)²³⁾.

(5) Sampling

The sample was taken from the effluent of the continuous system. The dissolved phosphorus and total iron concentration samples were immediately filtered using 0.20 µm syringe filter.

(6) Analysis

The concentration of phosphorus and iron compounds in solution samples were measured by using a UV-Vis spectrophotometer (DR 3900, HACH Co., USA) via USEPA PhosVer 3 (Ascorbic acid method) at 880 nm and TPTZ (2,4,6-Tri (2-pyridinyl)-1,3,5-triazine) method at 590 nm, respectively²³⁾. For further analysis, copper concentration was measured by Bathocuproine method at 478 nm. The sample pH and oxidation and reduction potential (ORP) were measured by portable pH meter (D-72, HORIBA, Ltd., Japan). The dissolved oxygen (DO) concentration was measured by portable DO meter (HQ30d-flexi, HACH, USA).

(7) Characterization of NZVI and NZVI/CuCl₂

Compositions of the iron products were analyzed by XRD (TTR, Rigaku, Tokyo, Japan). Samples were analyzed using Cu Kα radiation (λ = 1.5418 Å) with a scan rate of 2° min⁻¹ and scanning range between 3° and 90°. The surface morphologies of synthesized particles were obtained on TEM (JEM-ARM 200F, JEOL Co., Japan).

(8) Calculation of overall removal efficiency

To evaluate this system, the overall removal efficiency was calculated after determining the Removed mass of phosphorus $R \cdot m_{PO_4^{3-}}$ (Equation (2)):

$$R \cdot m_{PO_4^{3-}} = (C_{inf} \cdot V(t) - \int_{C_{eff,sand} (no\ NZVI), t=0}^{C_{eff,sand} (no\ NZVI), t=t} C_t dV(t)) - \int_{C_{eff}, t=0}^{C_{eff}, t=t} C_t dV(t) \quad (2)$$

where $R \cdot m_{PO_4^{3-}}$ is evaluated by subtracting phosphorus effluent mass (the integral part) from the total inlet phosphorus mass; $C_{inf} \cdot V(t)$ as C_{inf} is the concentration of phosphorus at $t = 0$; and V is the volume treated at a certain time t . The phosphorus mass captured by sand column (the first integral part) in the absence of NZVI was subtracted from the inlet phosphorus mass in advance. The second integral part was estimated using the trapezoidal rule starting from initial concentration to final desired concentra-

tion that contained the target region. After that, the overall phosphorus removal efficiency was calculated by dividing the total phosphorus mass carried in the water flow³³.

3. RESULTS

(1) Characterization of the synthesized particles

The composition of synthesized particles was observed by analyzing the XRD pattern. **Figure 2** shows the NZVI and NZVI/CuCl₂ bimetallic particles. **Figure 2(a)** shows the main peak of intensity at 44.8°, 2θ indicating the presence of zero valent iron in the synthesized nanoscale iron materials. **Figure 2(b)** shows the main peaks of intensity at 44.8°, 2θ, and 65.8°, respectively, and the detected zero valent iron, copper, and copper iron oxide. According to this results, copper existed on the surface of NZVI as determined by the following equation 3:

This suggested that copper existed on the NZVI surface and could be defined as bimetallic NZVI/CuCl₂.

Figures 3(a) and **3(b)** show the TEM images of NZVI and NZVI/CuCl₂. NZVI particles showed a chain-structure form due to the agglomeration. By contrast, bimetallic particles relatively distributed separately owing to the coating by copper. Additionally, the TEM images indicated that both synthesized particles were generally spherical and nano-scale. The estimated one particle size from the TEM images was around 100 nm for both samples.

Fig. 2 The XRD pattern of NZVI (a) and NZVI/CuCl₂ (b).

(2) The filtration effect of measuring phosphorus

The phosphorus adsorbed on the surface of NZVI must be considered to measure the phosphorus concentration accurately. Especially, the filtration before the measurement might affect the results. To check this effect, a small batch experiment was conducted and measured the phosphorus concentration after finishing the batch experiment by non-filtration and filtration. **Figure 4** shows the difference in phosphorus concentrations using different sampling methods. The non-filtration and filtration phosphorus concentration were 26.70 ± 0.32 and 26.48 ± 0.24 mg P/L, respectively. According to these results, there were no significant differences between them. After this section, all phosphorus concentration were measured by filtration method.

Fig. 3 The TEM images of NZVI (a) and NZVI/CuCl₂ (b).

Fig. 4 The difference in phosphorus concentrations using different sampling methods (Initial P concentration: 50 mg P/L, Solution volume: 250mL, Initial NZVI dosage: 250mg, Reaction time: 3h, Anoxic, Temperature: 25°C).

(3) The removal performance of the continuous system

a) The phosphorus removal efficiency of each unit

Figure 5 shows the phosphorus concentration profiles obtained from each unit. Only the result of experiment 1 is shown in this section.

This result suggested that the phosphorus was removed mainly at the CSFR. Within the first three hours, high phosphorus removal efficiency was obtained from all units. After that, phosphorus concentration increased with time until the end of the experiment.

Figure 6 shows the phosphorus overall removal efficiency calculated by equation 2. When calculating the values of the first three units, the first integral part was not considered. The phosphorus was mainly removed at CSFR and removal efficiency was achieved at 73.84%.

As mentioned in Chapter 2, CSFR corresponded to the main reactor. From this calculation, the role of the CSFR was verified. At the settler and polishing unit, the phosphorus was slightly removed and the removal efficiency was achieved up to 75.20% and 77.44%, respectively. With respect to the sand column, overall removal efficiency up to 81.89% was achieved, considering the first integral.

Fig. 5 The profile of phosphorus concentration.

Fig. 6 The phosphorus overall removal efficiency.

b) The total iron removal efficiency of each unit

Figure 7 shows the total iron concentration profiles obtained from CSFR and settler. Only the result of experiment 1 result is shown in this section. With respect to the CSFR, there were significant differences between total (non-filtration) and soluble (filtration). It is because the NZVI particles were out-flowed directly to the settler. But with respect to the settler, there was no significant change between the total and soluble samples. This result suggested that almost particles were sedimented at the settler.

Figure 8 shows the total iron concentration profiles obtained from the polishing unit and sand column. There were no significant differences between total and soluble samples obtained from both units.

Fig. 7 The profile of total Fe concentration (CSFR and settler).

Fig. 8 The profile of total Fe concentration (Polishing unit and sand column).

Fig. 9 The total Fe overall removal efficiency.

Figure 9 shows the total iron overall removal efficiency.

At the settler, 80.62% of total iron was sedimented and recycled to the CSFR. With respect to the polishing unit, the total iron removal efficiency of 97.71% was achieved. Finally, the highest removal efficiency of 99.05% was obtained from the sand column. These results strongly indicated that the role of each unit was achieved as mentioned in Chapter 2.

c) The relationship between phosphorus concentration and total iron concentration

Figure 10 shows the profile of the phosphorus and total iron concentration obtained from CSFR in experiment 1. With respect to the total iron concentration, it was approximately 2,500 mg Fe/L at the beginning of the experiment. However, it decreased with time to until about 1,000 mg Fe/L. On the other hand, phosphorus concentration increased with time.

Figure 11 shows the relationship between phosphorus concentration and total iron concentration. The correlation coefficient was $R^2 = 0.7965$. The negative correlation was confirmed between these parameters. These results suggested that phosphorus concentration increased when the iron concentration decreased. These results also indicated that monitoring phosphorus concentration and total iron concentration might be useful to maintain the system.

Fig. 10 The profile of the phosphorus and total Fe concentration (CSFR, experiment 1).

Fig. 11 The relationship between the phosphorus and total Fe concentration (CSFR, experiment 1).

d) The relationship between phosphorus concentration and ORP value

Figure 12 shows the profile of the phosphorus concentration and ORP value obtained from CSFR in experiment 1. With respect to the ORP value, it was approximately -250 mV at the beginning of the experiment. But it increased to a positive value with time. Similarly, the phosphorus concentration also increased with time. **Figure 13** shows the relationship between phosphorus concentration and ORP value.

The correlation coefficient was $R^2 = 0.7599$. The positive correlation was confirmed between these parameters in this case. These results suggested that phosphorus removal mechanisms mainly occurred when the ORP value was around -250 mV. And when the ORP value increased, the phosphorus concentration increased simultaneously. These phenomena suggested that the ORP value would be one of the parameters to decide the new NZVI dosage timing.

e) The relationship between total iron concentration and ORP value

Figure 14 shows the profile of the total iron concentration and ORP value obtained from CSFR in experiment 1. With respect to the ORP value, it was approximately -250 mV at the beginning of the experiment and the highest total iron concentration was confirmed at that time. **Figure 15** shows the relationship between the total iron concentration and ORP value. The strong correlation coefficient of $R^2 =$

Fig. 12 The profile of the phosphorus concentration and ORP value (CSFR, experiment 1).

Fig. 13 The relationship between the phosphorus concentration and ORP value (CSFR, experiment 1).

Fig. 14 The profile of the total Fe concentration and ORP value (CSFR, experiment 1).

Fig. 15 The relationship between the total Fe concentration and ORP value (CSFR, experiment 1).

Fig. 16 The TEM images of the spent NZVI with different resolution ((a): 20 nm, (b): 50 nm, (c): 100 nm, CSFR, experiment 1).

Fig. 17 The TEM images of the spent NZVI with different resolution ((a): 20 nm, (b): 50 nm, (c): 100 nm, Settler, experiment 1).

Fig. 18 The TEM images of the spent NZVI with different resolution ((a): 20 nm, (b): 50 nm, (c): 100 nm, Polishing unit, experiment 1).

0.9969 was obtained. The negative correlationship was confirmed between these parameters in this case. These results strongly indicated that ORP value would be an important monitoring parameter in this experiment.

f) The TEM images of spent NZVI particles

Figures 16, 17, and 18 show the TEM images of spent NZVI particles obtained from CSFR, settler, and polishing unit. All particles showed complex structure compared with the fresh one. Furthermore, all particle sizes appeared larger than nanosize due to adsorption, agglomeration, and oxidation.

(4) Effect of gaseous phase conditions on phosphorus removal

Regarding pH (Fig. 19), there was no significant difference between the three conditions in the initial three hours, and all results showed alkaline pH of around 8.5 to 9.9. However, after 12 hours, the pH of the ambient condition showed a maximum of 9.9. Also, the pH under aerobic condition decreased, while there was no significant change under anaerobic condition.

Regarding ORP and DO (Fig. 20), the ambient ORP value drastically decreased from -100 mV to -180 mV in the first 12 hours due to the phenomena that were explained in Chapter (3)-d. On the other hand, aerobic ORP value slightly increased.

Regarding total iron concentration (Fig. 21), all values fluctuated. It was suggested that the pathway of the water body affected the removal performance of total iron. However, all values showed less than around 4 mg Fe/L. From the Japanese regulation³²⁾, the capable total soluble iron concentration discharged to the environment was below 10 mg Fe/L. From these results, it is suggested that the system has enough ability to remove phosphorus with less soluble iron than the Japanese standards before being discharged to the environment.

Figure 22 shows the phosphorus removal efficiency profile. In the first three hours, all conditions achieved very high removal efficiency. The ambient, aerobic, and anaerobic removal efficiency rates were $96.30 \pm 1.65\%$, $98.88 \pm 0.47\%$, and $97.91 \pm 2.07\%$, respectively.

(5) Effect of CuCl_2 on phosphorus removal

Regarding pH (Fig. 23), the pH value of experiment 4 and experiment 5 was slightly low due to the CuCl_2 . In experiment 4, the pH value was maintained at a constant level for the whole duration.

Regarding ORP (Fig. 24), the experiment 4 ORP value was also maintained at a constant level similar to the pH value result. On the other hand, the experiment 5 ORP value drastically decreased from -40 mV to -120 mV after 12 hours.

Regarding total iron concentration (**Fig. 25**), experiment 4 and 5 values were less than around 1.5 mg Fe/L.

Figure 26 shows the phosphorus removal efficiency profile. In the first three hours, all conditions achieved very high removal efficiency similar to those in experiments 1-3.

Figure 27 shows the profile of copper concentration existing in the final effluent. From the Japanese regulation³²⁾, the capable copper concentration discharged to the environment was below 3 mg/L. This result strongly indicated that copper could be removed by the system sufficiently and it would not affect the animals in the natural water.

Fig. 19 The profile of the pH value (Measuring point: Settler).

Fig. 20 The profile of ORP value and DO concentration (Measuring point: Settler).

Fig. 21 The profile of the soluble total Fe conc. (Measuring point: Sand column).

Fig. 22 The profile of the phosphorus removal efficiency (Measuring point: Sand column).

Fig. 23 The profile of the pH value (Measuring point: Settler).

Fig. 24 The profile of ORP value and DO concentration (Measuring point: Settler).

Fig. 25 The profile of the soluble total Fe conc. (Measuring point: Sand column).

Fig. 26 The profile of the phosphorus removal efficiency (Measuring point: Sand column).

Fig. 27 The profile of the copper concentration (Measuring point: Sand column).

4. DISCUSSION

(1) The phosphorus removal mechanisms and overall removal efficiency

Table 2 shows the comparison of the calculated overall removal efficiency for the initial 3 hours and 36 hours. Comparing experiments 1 to 3, the highest removal efficiency was obtained from experiment 2 (aerobic). As mentioned in the introduction part, the main mechanisms for removing phosphorus were adsorption and coprecipitation. When NZVI was added to water, NZVI corroded and Fe^{2+} ions eluted (Equation (4)). Particularly in the case of experiment 2 (**Fig. 28**), NZVI was oxidized into Fe^{2+} and then changed into Fe^{3+} (Equation (5)) in the presence of higher oxygen concentration.

Aerobic condition enhanced more iron corrosion to the nanoscale iron surface, which in turn helped in more phosphorus adsorption as ferric hydroxides (Equation (6)) and iron oxy (hydroxide) (Equation (7)) are good sorbents for contaminants²². Also, Fe^{3+} reacted with PO_4^{3-} directly and FePO_4 (Equation (8)) was formed on the iron surface, which could obtain highly efficient removal of phosphorus due to the

Table 2 Comparison of calculated overall removal efficiency for the initial 3 hours and 36 hours.

Exp. No.	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5
Gaseous phase	Ambient	Aerobic	Anaerobic	Ambient	Ambient
CuCl_2	-	-	-	Bimetal	Addition
Initial 3 hours removal effi. (%)	96.57	98.72	98.18	99.48	94.42
Overall removal effi. (%)	81.89	91.37	73.81	94.96	82.82

Fig. 28 Schematic image of phosphorus removal mechanisms.

relatively low K_{sp} constant of 1.3×10^{-22} ³⁴). As a result, the highest removal efficiency was obtained from experiment 2.

Fig. 29 The XRD pattern of spent NZVI (Experiment 1, CSFR).

Fig. 30 The phosphorus removal mechanisms under different pH^(11), 22).

Fig. 31 The profile of the copper concentration (Measuring point: CSFR).

Fig. 32 The relationship between effluent volume and phosphorus concentration (Measuring point: Sand column).

Figure 29 shows the XRD pattern of spent NZVI. The FePO_4 peaks appeared at 25.4° , 2θ . This result strongly indicated that coprecipitation occurred in the CSFR and it was more favorable in this system.

Comparing experiments 1, 4, and 5, the highest overall removal efficiency was obtained from experiment 4 (CuCl_2 bimetallic). The bimetallic particles could provide more active site on the surface of nanoparticles and phosphorus could be adsorbed easily⁽²⁸⁾. And also some researchers have reported that acidic pH enhanced the phosphorus adsorption^(11), 21) (Fig. 30). It was because the isoelectric point (IEP) of CuCl_2 bimetallic NZVI was 7.3⁽³⁶⁾.

When the solution pH was lower than IEP, the particle surface became positively charged, which made the surface suitable for anion (PO_4^{3-}) sorption. On the other hand, when the solution pH was higher than IEP, both adsorbent and adsorbate became negatively charged, leading to enhanced electric repulsion between them⁽¹¹⁾. Moreover, the phosphorus anions and OH^- ions would compete to get active site, thus the adsorption efficiency would be decreased⁽³⁷⁾. In the bimetallic case, the addition of CuCl_2 increases H^+ ions as shown in the following reaction (Equation (9), (10)):

From Fig. 23, it can be seen that the pH values of experiments 4 and 5 were lower than those in experiment 1. Especially, the pH value of experiment 4 was the lowest. It suggested that discharged H^+ ions decreased the pH values of the solution and enhanced more adsorption. It was expected that bimetallic particles would increase phosphorus removal by providing active sites. However, the function as an oxidant which eluted H^+ was obtained at the same time.

In experiment 5, CuCl_2 was added to CSFR before the start of operation. Eljamal et al.⁽²³⁾ reported that maximum adsorption capacity by NZVI/ CuCl_2 (addition) was enhanced with 50 mg P/g. However in this case, significant advantage was not confirmed by just adding CuCl_2 . Figure 31 shows the profile of the copper concentration existing in the effluent of CSFR. The main assumption for the addition of copper was that of enhancing iron corrosion. The results showed that higher copper outflowed from CSFR at the beginning of experiment 5.

The result also suggested that copper outflowed before proper reaction from CSFR could start. Hence it is suggested that copper addition is not suitable for the continuous system.

From the calculated overall removal efficiency and other data, significant changes could not be obtained from experiments 2 and 4. Finally, to determine the best condition in this study, the relationship

between phosphorus concentration and treated volume is shown in **Fig. 32**.

This result shows that the bimetallic condition could treat large volume phosphorus solution compared with the aerobic one and it could lead to minimization of reactors and systems, which would be a strong advantage when scaling up this system. From these results, we concluded that bimetallic condition is the best condition to remove phosphorus using this system.

(2) The advantage and disadvantage of NZVI continuous system

This section shows the advantage and disadvantage of NZVI continuous system obtained through this study.

a) Advantage

More than 99% excellent phosphorus overall removal efficiency was obtained from aerobic and bimetallic case in the first three hours. This is the most important advantage obtained from this experiment. This result suggested that NZVI could start removing phosphorus immediately after dosing it to the water. For example, the biological technique needs time to accumulate bacteria.

b) Disadvantage

The problem with NZVI is that it does not last long. More than 95% removal efficiency could be obtained only in the initial three hours. After the removal efficiency decreases, a new NZVI dosing will be necessary.

5. CONCLUSION

The main purpose of this study was to develop and evaluate phosphorus removal system using NZVI particles. The continuous experiment showed that 73.84% phosphorus was removed mainly at CSFR. And 80.62% total iron was removed and recycled at the settler. On the basis of the continuous operation results, there was a strong relationship between iron concentration and ORP value ($R^2 = 0.9969$). This result indicated that ORP would be an important monitoring parameter while operating continuous systems. The aerobic condition contributed the highest phosphorus overall removal efficiency (91.37%) due to the enhancement of iron corrosion. Also, copper bimetal particles achieved the highest removal efficiency (94.96%) due to increase in active site and decrease in solution pH. Finally, comparing the aerobic and bimetallic cases, we concluded that the bimetallic case was the best condition for removing phosphorus because the bimetallic condition could treat large solution volume than the aerobic one could.

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